

[54] **ELECTROCHEMICAL MEASURING CELL HAVING AN ANCILLARY ELECTRODE**

[75] **Inventor:** Uvo Hölscher, Stockelsdorf, Fed. Rep. of Germany

[73] **Assignee:** Dragerwerk Aktiengesellschaft, Lübeck, Fed. Rep. of Germany

[21] **Appl. No.:** 866,578

[22] **Filed:** May 22, 1986

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 771,995, Sep. 3, 1985, Pat. No. 4,624,261.

[30] **Foreign Application Priority Data**

Sep. 7, 1984 [DE] Fed. Rep. of Germany 3432950

[51] **Int. Cl.⁴** A61B 5/04; G01N 27/52

[52] **U.S. Cl.** 128/635; 128/639; 128/644; 128/670; 204/403; 204/412; 204/415

[58] **Field of Search** 204/403, 412, 415, 1 P; 128/635, 639, 644, 670

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,468,781	9/1969	Lucero	204/415
3,708,412	1/1973	Lofgren	204/415
4,517,982	5/1985	Shiga et al.	128/635
4,538,617	9/1985	Jensen	128/635

FOREIGN PATENT DOCUMENTS

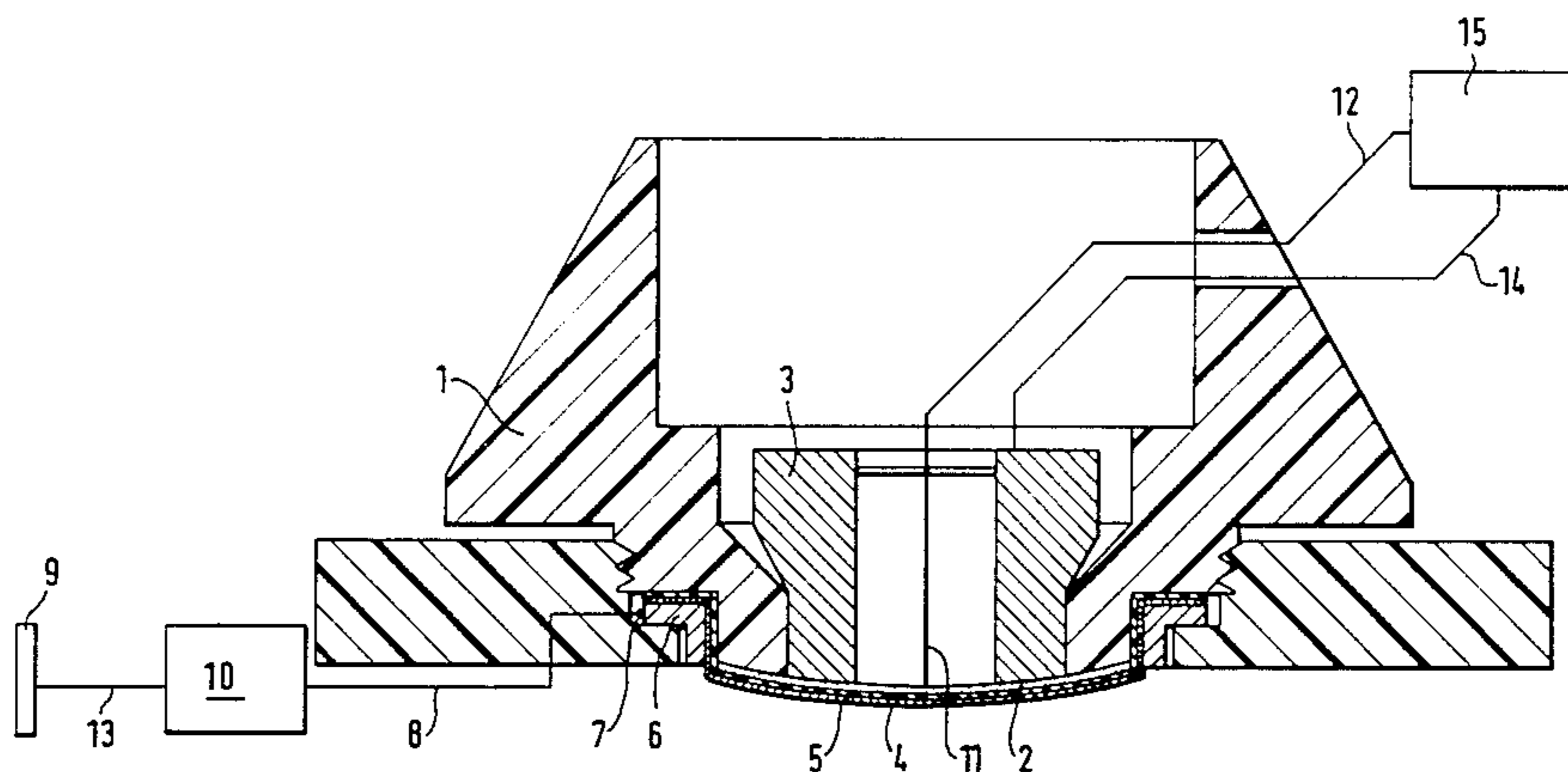
0077054	10/1982	European Pat. Off.	128/635
2930663	2/1981	Fed. Rep. of Germany	128/635
54344	5/1981	Japan	204/415
56748	4/1982	Japan	204/415

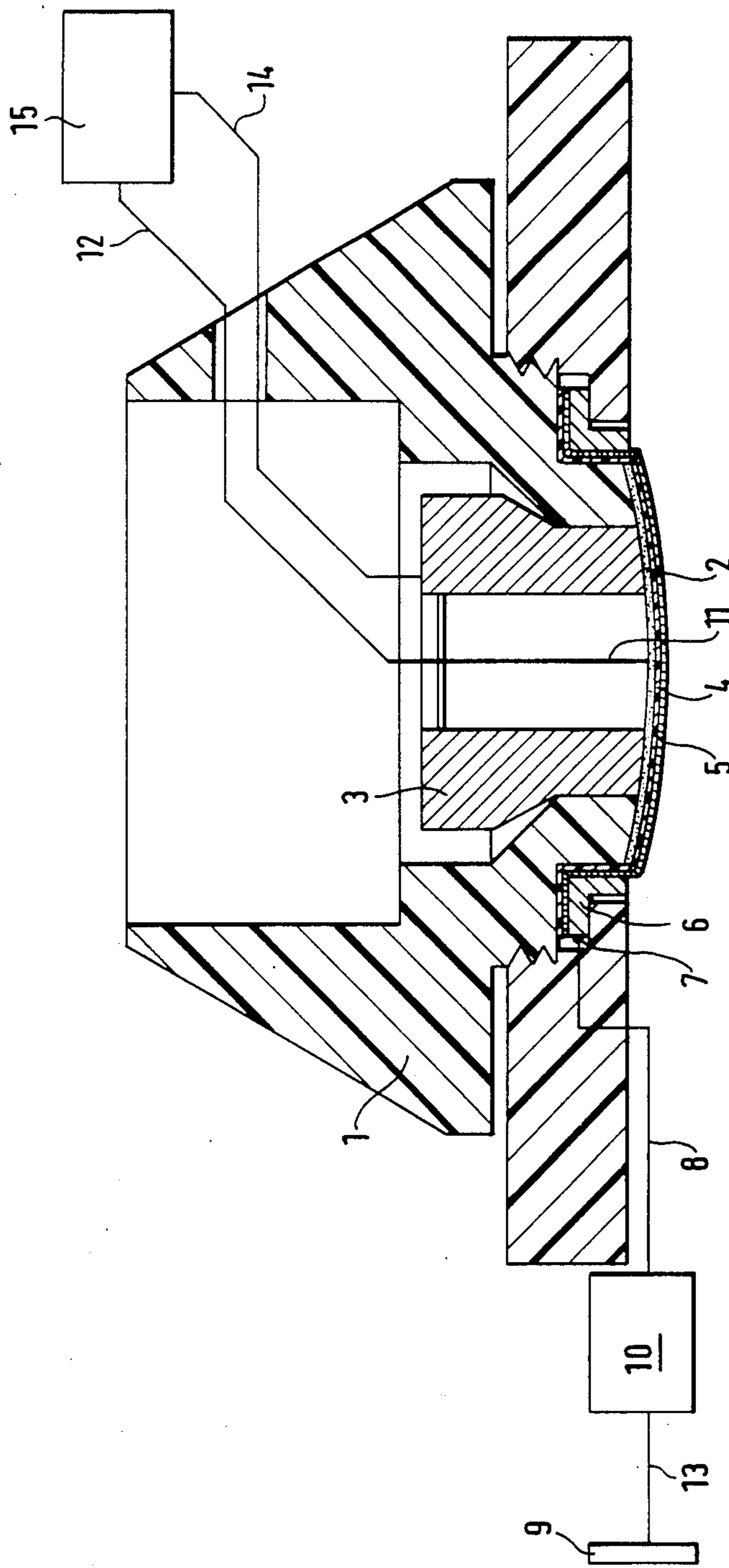
Primary Examiner—T. Tung
Attorney, Agent, or Firm—Walter Ottesen

[57] **ABSTRACT**

An electrochemical measuring cell is disclosed having a device for sensing an external electrical potential. The device is arranged in the region of the outer surface of the diffusion membrane of the cell. The device can be, for example, in the form of a conductive, gas-permeable coating applied to the outer surface of the diffusion membrane.

6 Claims, 1 Drawing Figure





ELECTROCHEMICAL MEASURING CELL HAVING AN ANCILLARY ELECTRODE

RELATED APPLICATION

This is a continuation-in-part of the application Ser. No. 771,995 filed on Sept. 3, 1985, now U.S. Pat. No. 4,624,261, and entitled "Electrochemical Measuring Cell having an Ancillary Electrode".

FIELD OF THE INVENTION

The invention relates to an electrochemical measuring cell which includes a counter electrode and a measuring electrode disposed in an electrolyte. The electrolyte is separated from the ambient by means of a diffusion membrane. The electrochemical measuring cell further includes an arrangement for additionally sensing an external electrical potential.

BACKGROUND OF THE INVENTION

An electrochemical measuring cell of the above type is disclosed in European patent application No. A2 0077054. This measuring cell includes a first electrode arrangement which is sealed off with respect to the ambient by means of a diffusion membrane. The first electrode arrangement is surrounded by a second annular electrode with the corresponding counter electrode mounted on the rearward end of the head of the measuring cell. The ancillary electrode arrangement can, for example, be utilized to record bio-electrical quantities (Electrocardiogram).

In the known transducer, the ancillary annular electrode is held in a threaded ring disposed in surrounding relationship to the measuring head. Consequently, the measuring cell has such a size that it is unsuitable for placement in smaller openings. Furthermore, with the overall size otherwise being the same, the adhering surface for attaching the measuring cell to a support such as the skin of a person or the hide of an animal is reduced in such a manner that a reliable adherence is no longer assured for difficult conditions which often occur in practice.

SUMMARY OF THE INVENTION

It is an object of the invention to improve the known transducers so that a device for additionally sensing an external electrical potential can be mounted on the measuring cell without taking up space for itself thereby increasing the available adhering surface.

The above object is realized in that the device is mounted in the outer surface region of the diffusion membrane.

With the arrangement of the device pursuant to the invention, a large surface electrode for sensing an external electrical potential is provided. By placing the device in the region of the diffusion membrane, a utilization of surface is achieved which is subtle in its application.

In an advantageous embodiment of the invention, the device can be a coating which is applied to the outer surface of the membrane and can, for example, be a metal or graphite layer with a wire mesh or grid made of conductive material embedded therein.

It is desirable to prevent polarization at the interface region between the electrolyte and the coating as this will introduce voltage errors in the dc potential taken off at the coating. Such polarization or electrode "noise" introduces errors which can prevent accurate

measurements from being made, for example, in the recording of an electrocardiogram. The phenomenon of electrode noise is described, for example, in an article entitled "Electrode Potential Stability" by S. Aronson and L. A. Geddes in the Proceedings of the IEEE, pages 987 and 988 (1985). Also, reference may be made to "Elektroenzephalographie, Technik und Methoden" by R. Cooper, J. W. Osselton and J. C. Shaw, pages 15 to 30, Gustav Fischer Verlag (1984).

A pure silver coating has been found to yield sufficiently unpolarized signals for especially sensing bio-electrical quantities. When this electrode is applied to the human skin, the chlorine content of the surface of the skin will chlorinate the electrode material (silver), and will stabilize it during use.

The sensitivity of the silver-coated membrane can be improved by halogenating the silver during manufacture of the electrode by exposing the same to a solution of halogenated salt and conducting a current through it.

Minimum polarization and most effective sensitivity can be verified as the silver coating is chlorinated.

In a further advantageous embodiment of the invention, the diffusion membrane itself can be made of a conductive plastic. Such a conductive plastic is preferably polypyrrole. However, there are also other known conductive plastics which can be used. In addition, if such conductive plastics comprise electrochemically active substances or are themselves electrochemically active, such a diffusion membrane can at the same time serve as the measuring electrode of the electrochemical cell.

BRIEF DESCRIPTION OF THE DRAWING

The drawing consists of one FIGURE showing an elevation view, partially in section, of an embodiment of the electrochemical measuring cell of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The electrochemical measuring cell includes a housing 1 which contains the electrolyte 2 and the counter electrode 3. The housing 1 is sealed off with respect to the ambient by a diffusion membrane 4. An electrically conductive coating 5 is applied to the outer surface of the diffusion membrane 4. The diffusion membrane can be made of a material such as plastic and thereby define a smooth flat-like outer surface for receiving the coating 5 thereon.

In addition to being electrically conductive, the coating 5 is permeable to gas and can be made of pure silver. Another suitable material is halogenated (chlorine, bromine, iodine) silver of which chlorinated silver is especially suitable. Because the outer surface of the diffusion membrane 4 is smooth, the particles making up the coating are in physical and electrical contact with each other over this surface thereby ensuring a reliable transmission of potentials along the coating.

The coating 5 extends so far that the clamping ring 6 is in electrical contact with the coated diffusion membrane 4 so that the external electrical potential can be taken off on the clamping ring 6, and conducted via the contact 7 and the lead 8 to an evaluation unit 10. A second measuring input of the evaluation unit 10 is connected via a connecting lead 13 to a reference electrode 9. The measuring electrode 11 is connected with the measuring device 15 via lead 12 and the counter electrode 3 is connected with the measuring device 15

via lead 14 so that the measuring device 15 can evaluate the measuring signals of the electrochemical cell.

It is understood that the foregoing description is that of the preferred embodiments of the invention and that various changes and modifications may be made thereto without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

- 1. An electrochemical measuring cell comprising:
 - an electrolyte;
 - a measuring electrode disposed in said electrolyte;
 - a counter electrode also disposed in said electrolyte;
 - a housing for holding said electrolyte;
 - a diffusion membrane for separating said electrolyte from the ambient and having a smooth outer surface facing away from said electrolyte; and,
 - an electrically-conductive, gas-permeable coating of silver applied to said outer surface for sensing an external electrical potential.
- 2. The electrochemical measuring cell of claim 1 comprising electric circuit means mounted on said housing for conducting said external potential away

from said coating and making the same accessible for measurement.

- 3. An electrochemical measuring cell comprising:
 - an electrolyte;
 - a measuring electrode disposed in said electrolyte;
 - a counter electrode also disposed in said electrolyte;
 - a housing for holding said electrolyte;
 - a diffusion membrane for separating said electrolyte from the ambient and having a smooth outer surface facing away from said electrolyte; and,
 - an electrically-conductive, gas-permeable coating made of a halogenated compound of silver applied to said smooth outer surface.
- 4. The electrochemical measuring cell of claim 3, wherein the halogen of said halogenated compound of silver is selected from the group consisting of chlorine, bromine and iodine.
- 5. The electrochemical measuring cell of claim 3, said coating consisting of chlorinated silver.
- 6. The electrochemical measuring cell of claim 3 comprising electric circuit means mounted on said housing for conducting said external potential away from said coating and making the same accessible for measurement.

* * * * *

30

35

40

45

50

55

60

65

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,681,115
DATED : July 21, 1987
INVENTOR(S) : Uvo Hölscher

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the front page, under Assignee: delete "Dragerwerk" and substitute -- Drägerwerk -- therefor.

In the Abstract, line 2: delete "electical" and substitute -- electrical -- therefor.

In column 4, line 11: delete "cotating" and substitute -- coating -- therefor.

**Signed and Sealed this
Fifth Day of January, 1988**

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks